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## Statement of the Problem Studied

The quest for new materials that meet the specialized demands of high technology and biomedicine has spurred the synthesis of many new polymers. The most diverse set of these is unquestionably a class of inorganic polymers known as polyphosphazenes,  $[R_2PN]_n$ . The almost limitless variation in the substituents along the backbone affords a series of polymers with an incredibly broad spectrum of properties and ultimate applications including elastomeric, electronic, optical, protective, biomedical, membrane, and textile materials.

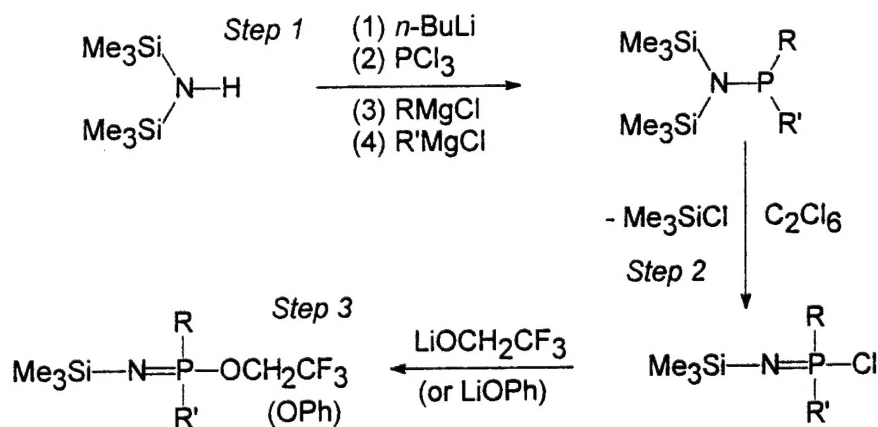
To date, two problems appear to have limited the broad commercialization of polyphosphazenes. The first is what is perceived as a problematic synthesis of these polymers. The two main approaches that have been developed are ring-opening substitution and condensation polymerization, but only the former has been used by U. S. industry. This involves the preparation of poly(dichlorophosphazene),  $[Cl_2PN]_n$ , by ring opening of the trimer,  $[Cl_2PN]_3$ , and subsequent substitution with electrophiles that primarily produce polymers with P-N and P-O bonded substituents. Condensation polymerization, on the other hand, has received little attention by industry, despite the versatility of substituents afforded by thermolysis of Si-N-P monomers. This is partly due to multi-step syntheses of the appropriate condensation monomers and to high polymerization energy needs. A second hindrance in further commercialization of polyphosphazenes has been the identification of applications for the unique properties of this system. Various aspects of both problems were investigated in the course of this contract period.

This program of research addressed several aspects of the poly(alkyl/arylphosphazenes). The *first* of these was the development of improved polymerization methods for consistent preparation of high molecular weight samples of the basic poly(alkyl/arylphosphazenes) on a large scale. *Secondly*, the chemistry of the precursors was studied to better understand the mechanism of the polymerization, to prepare potential precursors to other main group element containing polymers, and to prepare block copolymers. A *third* part of this work involved the studies of the reactivity of the poly(alkyl/arylphosphazenes) and the synthesis of new poly(phosphazenes) from the preformed polymers. *Finally*, a variety of properties of the poly(alkyl/arylphosphazenes) were investigated, including thermal and surface properties, and gas permeability. The details of each of these areas of research are given in the following sections.

## Summary of Research Findings

**Precursor Synthesis and Reactivity.** During the course of this ARO grant, several areas in this context have been under investigation at Texas Christian University. These include: (1) development of a simplified, "one-pot" synthesis of the N-silylphosphoranimine monomers; (2) synthesis and reactivity studies of related Si-N-P compounds as potential new polymerization monomers; (3) synthesis and structural characterization of sterically congested Si-N-P derivatives; (4) synthesis and derivative chemistry of new P-functionalized N-silylphosphoranimines including systems containing amino, acetylenic, or ether side groups on phosphorus; (5) Si-N bond cleavage reactions of the N-silylphosphoranimines with reactive halides such as phosphoryl chlorides; and (6) preparation of new "dimeric" phosphoranimines as potential precursors to polymers with well-defined side-group patterns.

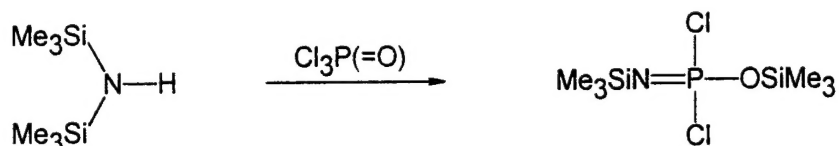
First, in the improved "one-pot" synthesis, the following series of reactions are carried out sequentially in the same reaction flask. In addition to greatly simplifying and reducing the cost of preparing precursors to homopolymers like  $[\text{Ph}(\text{Me})\text{PN}]_n$  and  $[\text{Me}_2\text{PN}]_n$ , this method has been recently used to directly prepare *mixtures* of precursors (e.g.,  $\text{R} = \text{Me}$ ;  $\text{R}' = \text{Et}$ ,  $n\text{-Pr}$ ,  $n\text{-Bu}$ ,  $n\text{-Hex}$ , etc.) by simply employing *mixtures* of two different Grignard reagents. Subsequent thermolysis affords the corresponding *random* copolymers.



Second, we conducted a two-pronged program aimed at simplifying the overall synthetic route to poly(alkyl/arylphosphazenes). In one phase, we studied the condensation polymerization (with or without catalysts) of *P-chlorophosphoranimines*,  $\text{Me}_3\text{SiN}=\text{PR}_2\text{Cl}$  in place of the more-difficult-to-prepare  $\text{P-OCH}_2\text{CF}_3$  derivatives. Preliminary results clearly demonstrated that the desired polyphosphazenes could be prepared in this manner, however, the polymerization

conditions and molecular weights ( $M_w \approx 10,000 - 30,000$ ) of the products were not fully optimized.

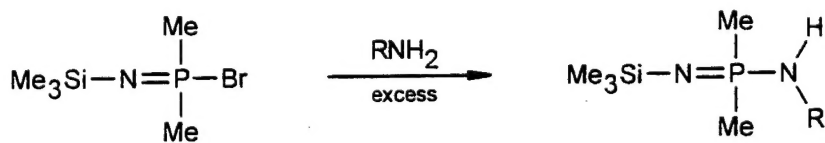
In the other phase, our objective was to prepare new polymer precursors *in one or two steps* directly from commercial reagents. For example, treatment of hexamethyldisilazane with  $\text{Cl}_3\text{P}(=\text{O})$  surprisingly afforded the P-siloxy-P,P-dichlorophosphoranimine derivative in nearly quantitative yield. Unfortunately, preliminary efforts to polymerize this compound or to derivatize it by way of nucleophilic substitution reactions at the P-Cl bonds met with limited success.



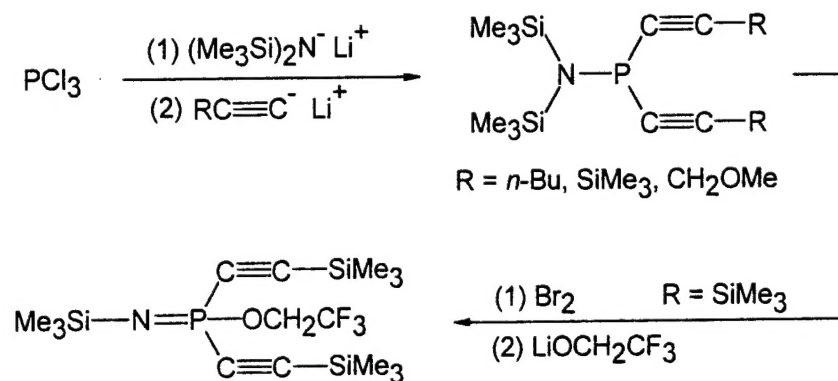
Third, a large series of sterically congested N-silylphosphoranimines,  $\text{R}_3\text{SiN}=\text{PR}_2\text{X}$ , [ $\text{R}_3\text{Si} = t\text{BuMe}_2\text{Si}$ ,  $\text{Et}_3\text{Si}$ ,  $t\text{BuPh}_2\text{Si}$ ;  $\text{X} = \text{Br}$ ,  $\text{Cl}$ ,  $\text{OCH}_2\text{CF}_3$ ,  $\text{OPh}$ ] and their (silylamino)phosphine precursors were prepared and fully characterized by NMR spectroscopy. This work also included structural characterization, by X-ray diffraction, of several of these new (silylamino)phosphines and N-silylphosphoranimines such as the following.



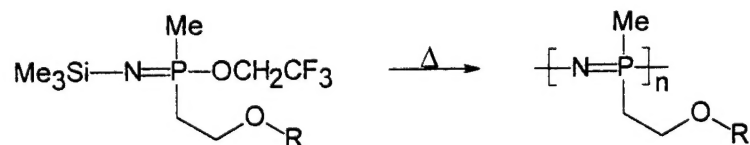
Fourth, several new types of N-silylphosphoranimines that contain various functional groups on phosphorus have been prepared and fully characterized. For example, in work aimed at the synthesis of novel oligomeric and polymeric  $-\text{N}=\text{P}-\text{N}-\text{E}-$  systems (e.g.,  $\text{E} = \text{B}$ ,  $\text{P}$ , or  $\text{S}$ ), we have prepared some new secondary amino derivatives of the bromophosphoranimines. Several new N-boryl derivatives of these phosphoranimines have been prepared via deprotonation of the N-H group, followed by treatment with various chloroboranes.



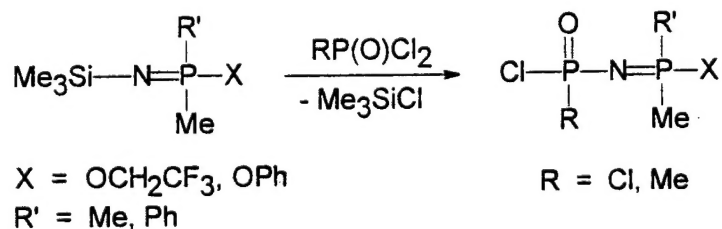
A series of Si-N-P compounds, such as the following, that contain acetylenic functional groups was also prepared and characterized. However, detailed thermolysis studies of these new P-acetylenic N-silylphosphoranimines have not yet been conducted.



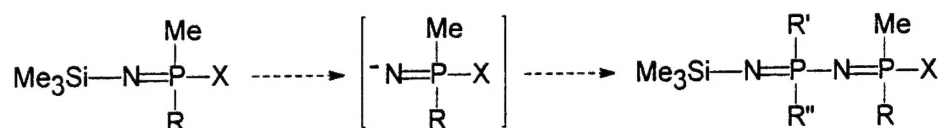
Other recent results in this area are based on continuing studies of deprotonation-substitution reactions of the pendent P-CH<sub>3</sub> groups in the precursors. By treatment of these precursor anions with  $\alpha$ -bromo ethers, we have prepared the first examples of N-silylphosphoranimine bearing alkyl ether side groups (R = Me, Et). Thermolysis of these precursors affords the corresponding homopolymers in which every monomer unit has an ether side group attached to phosphorus. Further studies of this reaction and properties of these novel polymers are in progress.



Fifth, we also investigated the reactivity of the Si-N bond in the polymer precursors. For example, the following series of novel N-phosphoryl derivatives were prepared and fully characterized by NMR spectroscopy and, in a few cases, X-ray diffraction as well.



Finally, we have recently developed straightforward methodology for the generation of phosphoranimine anions  $[\text{N}=\text{P}(\text{X})\text{R}_2]^-$  and for their conversion to a large series of new, acyclic phosphoranimine "dimers" as shown below. A few preliminary polymerization reactions have yielded novel *regular, alternating* copolymers such as  $[-\text{Me}_2\text{P}=\text{N}-\text{P}(\text{Ph})(\text{Me})=\text{N}-]_n$  in addition to several new 8-membered phosphazene ring systems. Three of these ring systems have been structurally characterized by X-ray diffraction, while property studies of the new polymeric materials are just beginning.

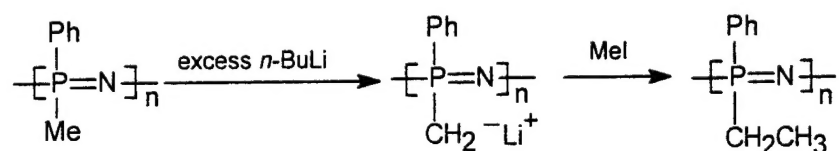


**Polymer Synthesis and Characterization.** The subcontract work supported by this ARO grant at Southern Methodist University focused on the synthesis and properties of polyphosphazenes that are derived from one simple, yet extremely versatile polymer, i.e., poly(methylphenylphosphazene),  $[\text{Me}(\text{Ph})\text{PN}]_n$ . The three sites of reactivity of this polymer were exploited to prepare new systems that were then used to establish structure-property relationships that are vital to the applications of poly(alkyl/arylphosphazenes). As described above, the synthesis of this "parent" polymer,  $[\text{Me}(\text{Ph})\text{PN}]_n$ , is now significantly more straightforward and consistent. The monomer is now prepared in a multi-step, one pot synthesis and distillation from molecular sieves provides monomer that consistently yields high molecular weight polymer with narrow molecular weight distributions. Moreover, the NaOPh catalyzed polymerization is complete in a matter of hours at moderate temperatures and the polymerization is readily done on large scales using benchtop glassware and techniques. It is also significant that  $[\text{Me}(\text{Ph})\text{PN}]_n$  is not only a starting point for the preparation of a variety of other polyphosphazenes, but is also a ready-to-use, air stable polymer with useful properties of its own.

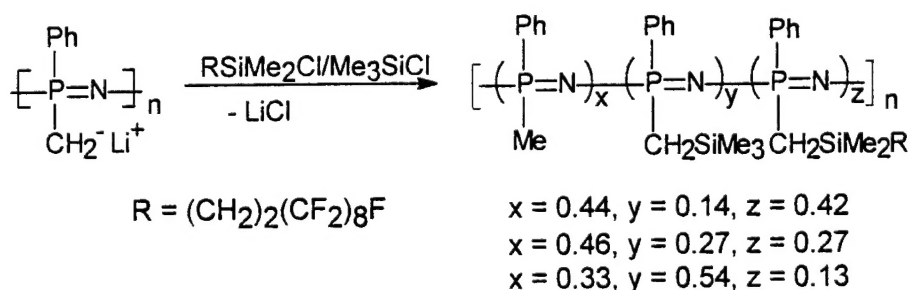
**Synthesis.** With the major goal of fine tuning the properties of the poly(alkyl/arylphosphazenes), studies of the synthetic diversity of the three reactive sites in  $[\text{Me}(\text{Ph})\text{PN}]_n$  were continued. As demonstrated previously, the primary site of interest was the methyl group where deprotonation-substitution reactions are straightforward and frequently accomplished in

one step. Long alkyl- or fluoroalkylsilyl, ketone, ether and polyether, and biphenyl ether groups were among many of the new moieties that were attached to the backbone through the PCH<sub>2</sub> linkage. Grafted side-chains of PMMA were also prepared by initiation of anionic polymerization of MMA by the deprotonated side groups of the polyphosphazene.

More significantly, we now better understand this important approach to new polymer systems. Using <sup>31</sup>P NMR spectroscopy, it was demonstrated that *all* of the methyl groups can be deprotonated with *n*-BuLi. Furthermore, small electrophiles such as MeI facilitate substitution of up to 95% of the deprotonated methyl side-groups, thus establishing that the degree of substitution in deprotonation-substitution reactions is a function of the size of the electrophile used to quench the intermediate anion sites.

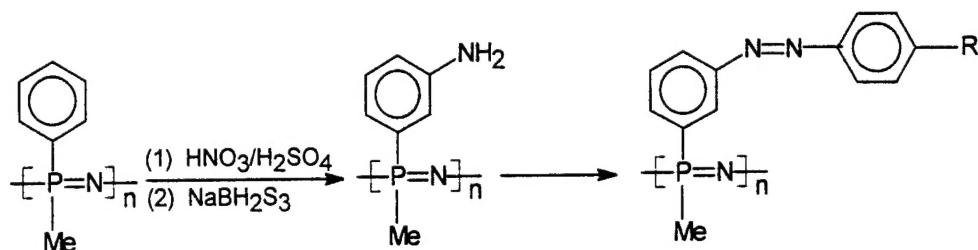


Similarly, the first co-substitution reactions of the deprotonated polymer system, as illustrated below, were also completed in the course of this work. These types of mixed-substituent polymers provide additional control and enhancement of properties such as glass transition temperatures and gas permeability (see Properties section below).



A second type of reactivity is offered at the phenyl group which can be substituted using the electrophilic aromatic substitution of nitro groups. With a better understanding of the strong basicity of the backbone nitrogen (see below), we found that pure samples of the nitrated polymer could be obtained reproducibly by using stronger bases (THF/water solutions of KOH or NaOH) to deprotonate the backbone after nitration in HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. The nitro group was reduced to an amino group and subsequently either converted to amides or used for diazonium coupling reactions.

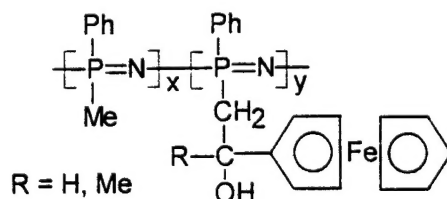




The third and somewhat unique reactive site in  $[\text{Me}(\text{Ph})\text{PN}]_n$  is the backbone nitrogen. Although the coordinating ability of this basic nitrogen hampers attachment of organometallic and metallic groups, we complexed mono-coordinating metals, (i.e.,  $\text{Ag}^+$  and  $\text{Li}^+$ ) without crosslinking the polymers. Moreover, the  $^{31}\text{P}$  NMR spectral studies of these systems indicated mobility of the coordinated metals in solution at room temperature as evidenced by observation of only one signal rather than the two expected for phosphorus atoms adjacent to and removed from coordinated nitrogen atoms. At low temperature ( $-90^\circ\text{C}$ ) the movement of the cations stopped. The backbone was also readily protonated with acetic and hydrochloric acid and the parent polymer was recovered without chain degradation by treatment with base.

*Properties.* A variety of properties of the poly(alkyl/arylphosphazenes) and their derivatives were also investigated. The glass transition temperatures of all the new systems were obtained and elemental analysis and NMR spectroscopy was used to determine that *all property measurements were performed on pure samples* to assure the accuracy and consistency of the data. The  $T_g$  values were correlated to free volumes which were calculated based on density measurements performed on many of these polyphosphazenes. The gas permeabilities, surface wettability, electrochemistry, adsorption of protein, and simple mechanical integrity of select systems were also studied and are discussed below.

Electrochemical studies of ferrocene polymers demonstrated completely reversibly electrochemistry by cyclic voltametry. The diffusion coefficients of these systems were high and charge-transfer efficiency increased as the degree of ferrocene substitution increased.



The surface wettability of the polyphosphazenes was also studied using contact angle measurements. While the parent polymer  $[\text{Me}(\text{Ph})\text{PN}]_n$  has a contact angle of only  $73^\circ$ , the polymers become significantly more hydrophobic with incorporation of alkylsilyl ( $90$  to  $97^\circ$ ) and fluoroalkylsilyl ( $97$  -  $101^\circ$ ) groups, e.g.,  $[\text{Me}(\text{Ph})\text{PN}]_x[\text{RMe}_2\text{SiCH}_2(\text{Ph})\text{PN}]_y$ . The contact angles of other fluorinated derivatives  $\{\text{Me}(\text{Ph})\text{PN}\}_x\{[\text{RR}'\text{C}(\text{OH})](\text{Ph})\text{PN}\}_y$  ( $\text{R} = \text{CF}_3$ ,  $\text{C}_6\text{F}_5$ , or  $\text{CF}_2\text{CF}_3$ ) were also be consistently higher ( $81$ - $92^\circ$ ) than the parent polymer,  $[\text{Me}(\text{Ph})\text{PN}]_n$ .

The gas permeabilities of membranes of these polymers were determined at  $35^\circ\text{C}$  and compared to that of the parent polymer  $[\text{Me}(\text{Ph})\text{PN}]_n$  for which permeabilities to  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$  were  $0.6 \times 10^{-10}$ ,  $1.8 \times 10^{-10}$ ,  $0.7 \times 10^{-10}$ ,  $6.5 \times 10^{-10} \text{ cm}^3(\text{STP})\cdot\text{cm}^{-1}\text{cmHg}^{-1}\text{sec}^{-1}$ , respectively. The incorporation of the silyl groups generally increased permeabilities relative to  $[\text{Me}(\text{Ph})\text{PN}]_n$  without significant changes in selectivity. Polymers from the co-substitution reactions had as much as a 15-fold increase in gas permeabilities with selectivity ratios (e.g.,  $\alpha_{\text{CO}_2/\text{CH}_4} = 8.9$ ) similar to those of  $[\text{Me}(\text{Ph})\text{PN}]_n$ . The trimethylsilyl groups also increased the  $T_g$  values of the terpolymers relative to the simple derivative  $[\text{Me}(\text{Ph})\text{PN}]_x[\text{Me}_3\text{SiCH}_2(\text{Ph})\text{PN}]_y$ , thus providing for fine-tuning of both the mechanical and permeability properties of these systems. Several of these polymers have permeabilities/selectivities comparable to fluorinated silicones, but less than  $[(\text{CF}_3\text{CH}_2\text{O})_2\text{PN}]_n$ . The gas permeation properties of these polymers were correlated with the lengths and concentration of the side-groups and with the estimated free volumes of the side groups and the experimentally measured densities.

In view of the earlier studies, demonstrating that the simple poly(alkyl/aryl-phosphazenes) and several derivatives are non-toxic and non-hemolytic, some addition biocompatibility studies were conducted. This involved measurements of the binding of simple proteins to the polyphosphazenes using radioiodine labeling. Uptake of bovine albumin was found to be unusually low for parent polymer  $[\text{Me}(\text{Ph})\text{PN}]_n$  as well as for the fluorinated derivative  $\{\text{Me}(\text{Ph})\text{PN}\}_x\{[\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2(\text{Me}_2\text{Si})](\text{Ph})\text{PN}\}_y$ . While the latter appears to be unaffected by the extended exposure to aqueous media, the parent polymer is transformed from a transparent film to an opaque white film upon soaking in water for several days, a phenomenon suggesting reorganization of the polymer surface.

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### Report of Inventions

No patent applications were filed by the primary or sub-contractors during the report period.